

OPTICAL PROPERTIES OF CO₂ ICE AND CO₂ SNOW FROM ULTRAVIOLET TO INFRARED: APPLICATION TO FROST DEPOSITS AND CLOUDS ON MARS

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The planet Mars has a tenuous atmosphere which is ~97% carbon dioxide. The annual variation of atmospheric pressure is about 40% of the mean value of 6 mbar, with most of the variation due to condensation in the winter hemisphere, where radiative cooling lowers the temperature of the surface and/or atmosphere to below the equilibrium condensation point. Modelling of the heat balance of the Martian poles depends on the radiative properties of the CO₂ clouds and frost which in turn depend on the refractive index and absorption coefficient of bulk CO₂ ice as well as particle size distributions and dust optical properties. These optical properties must be known throughout the visible and near infrared as well as in the thermal infrared.

Warren[1] has reviewed measurements of the optical constants of CO₂ ice, which contain a large number of gaps and uncertainties. Calvin[2], using the scattering model of Hapke[3], has shown that the spectral reflectance calculated with the Warren[1] index estimates in the near infrared do not match with the spectra of laboratory frosts or the spectra returned by Mariner 7. Indications are, however, that the absorption of CO₂ ice is very low in the visible and near ultraviolet and between the strong absorption bands in the infrared. This increases the reflectance and reduces the emissivity of a surface of small particles since photons can pass through more particles and be scattered out of the surface before being absorbed. Using the optical properties from Warren[1] and radiative transfer models [4,5], Warren et al.[6] calculated the spectral albedo and emissivity of CO₂ snow from 0.2 to 25 μ m as a function of particle size and dust or water ice contamination. The differences with our more common experience with water snow are striking, with near infrared reflectance > 90% and thermal infrared emissivity < 20% in some spectral regions and for some particle sizes (water snow is 'black' in these regions). The strength of these effects is dependent on accurate knowledge of absorption between the strong bands, which is not now available.

Previous investigators have found it difficult to grow CO₂ ice in other than thin films. This is apparently due to frost-like non-equilibrium growth or to excessive thermal stresses, which cause clouding or cracking [7]. The imaginary index of refraction has therefore been poorly measured or not measured at all where linear absorption < 10 cm⁻¹. Among the existing measurements of the absorption of CO₂ ice in the regions of low absorption are those from 0.3 μ m to 1 μ m with impure ice and those from 2.5 μ m to 25 μ m with cracked and cloudy samples [7]. However Gaizauskas[8] succeeded in growing clear crystals of several millimeters thickness to measure the absorption bands near 7 μ m. Measurements have never been made beyond 25 μ m, between 1 μ m and 2.5 μ m except for the strong bands or between the strong ultraviolet absorption < 0.15 μ m and 0.3 μ m.

We have found that it is possible to grow large clear samples of CO₂ ice at Mars-like temperatures of 150K-170K if a temperature-controlled refrigerator is connected to an isolated two-phase pure CO₂

system. In this way, the system pressure adjusts to the equilibrium value dictated by the refrigerator temperature and the ice grows at a rate consistent with the gas supply. Samples of up to 18 cm³ have been grown from ultra-high purity gas in this way. We have designed a chamber for transmission measurements whose optical path between the 13mm diameter windows is adjustable from 1.6mm to 107mm. This will allow measurements of linear absorption down to $<0.01 \text{ cm}^{-1}$. The test chamber is thermally isolated from the lab by a large vacuum chamber and radiatively isolated from the walls of the large chamber by a low emissivity shield. The test chamber is instrumented internally with two platinum thermistors for temperature measurement. The spectral resolution will be provided from the vacuum ultraviolet to 4.8 μm by a half-meter grating monochrometer whose slit image is focused in the chamber center and on the following detector by mirror optics. Imprecision in the exact alignment of the test chamber on the cold finger required the construction of highly articulated mirror mounts. Sources for this part of the investigation include a UV discharge source, a tungsten-halogen lamp, a Xenon discharge lamp and an infrared glow rod. An intricate moving mirror system has been designed to provide a path around the test chamber for reference. The detectors include a photomultiplier tube for the UV, a silicon photodetector for the visible and NIR, and an indium-antimonide (InSb) detector for the IR. A few of the combinations of source-grating-filter-detector remain to be tested before measurements can begin. All the light sources are chopped and the detector outputs fed through a lock-in amplifier to reject background and minimize noise. A preliminary transmission spectrum of a thick sample of CO₂ ice in the near infrared is shown in Fig. 1.

The spectral region from 2.5 μm to 50 μm will be measured by a Fourier transform spectrometer. The absorption coefficient will be determined by a linear fit to the logarithm of the absorption at different optical path lengths for each wavelength. Measurements will be made at two distinct temperatures, so some estimate of the temperature variation of the coefficients can be made. It may also be possible to make sufficiently accurate measurements of the real index of refraction to help constrain the Kramers-Kronig analysis made by Warren[1].

Once the revised optical constants have been determined as a function of wavelength and temperature, they can be applied to spectral reflectance/emissivity models for CO₂ snow surfaces, both pure and contaminated with dust or water ice, using the delta-Eddington approach of Warren et al.[6] and/or the modified two-stream approach of Hapke[3]. It will be useful, also, to develop an infrared scattering-emission cloud radiance model (especially as viewed from near the limb) in order to develop a strategy for the identification of CO₂ cloud layers by the PMIRR (atmospheric infrared radiometer) instrument on Mars Observer.

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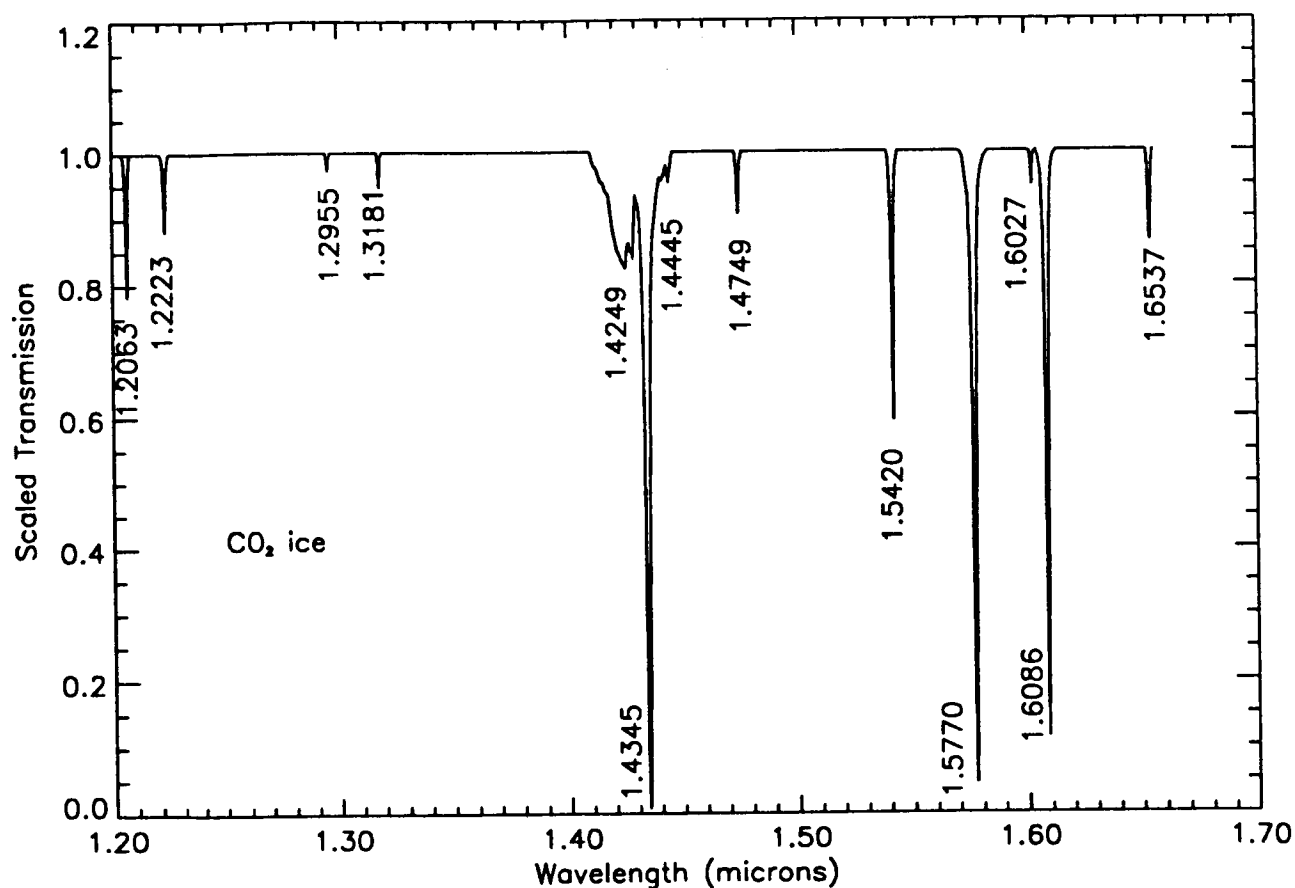


Figure 1: Preliminary absorption spectrum of a sample of CO₂ ice from 1.2 to 1.66 μm . The continuum background has been set arbitrarily to unity since its level is uncalibrated. The frequency calibration is based on the 1.4345 μm line shown in [1]. Note the unusual fine structure for a solid phase, with most lines only $\sim 2\text{nm}$ wide.